# Fundamental Studies of NOx Adsorber Materials

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## **Studies Performed to Date**

- Studies of Ba loading:
  - Morphology of the BaO storage material
  - Optimum morphology
  - Need for 'contact' with Pt?
  - What limits time to initial NOx 'breakthrough'?
- Variation of catalyst preparation:
  - Can time to 'breakthrough' be extended?
- Catalyst composition:
  - Variation in the storage material BaO, CaO, SrO, MgO
  - Variation in the support material acidic, basic, 'neutral'
- Mechanistic studies:
  - Reductive regeneration: nitrogen-balance experiments with production catalysts
  - NO oxidation: Pt particle-size dependence and deactivation



## Methods

- Synchrotron Temperature Programmed-XRD: catalyst structural changes (with Jon Hanson NSLS/Brookhaven National Lab)
- Transmission electron microscopy (TEM/EDX): morphological changes
- FTIR and NMR Spectroscopies, and Temperature-programmed desorption (TPD): surface chemistry
- Lab Reactor: performance measurements, kinetics and mechanisms











Evolution of LNT material morphology during preparation and use.

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Will very briefly show select pieces of data from these studies.



# Quantification of NOx uptake reveals small percentage of BaO used for storage



Assume  $Ba(NO_3)_2$  formation

Why so little?



### Calcination of 20%-BaO/Al<sub>2</sub>O<sub>3</sub>: TP-XRD



#### $Ba(NO_3)_2$ decomposition on $Al_2O_3$ : TP-XRD





## 20%-BaO/Al<sub>2</sub>O<sub>3</sub>, Calcined at 500 °C: TEM and EDS









Play Movie MorphCatalyst.wmv

Lean-NOx Trap (LNT) morphology changes shown in this 'movie' are based on the results of combined transmission electron microscopy (TEM), temperatureprogrammed desorption (TPD), FTIR and NMR spectroscopy, and synchrotron TP-XRD experiments.



### NO and NO<sub>2</sub> Desorption From BaO/Al<sub>2</sub>O<sub>3</sub> Following NO<sub>2</sub> Adsorption at 300K



Signatures of two 'forms' of nitrate?

#### F. Prinetto et al., JPC B 105(2001) 12732.

By combining FTIR and NO<sub>2</sub> TPD: 420 °C: decomposition of bidentate nitrates  $Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + 1/2O_2$ 500 °C: decomposition of ionic nitrates  $Ba(NO_3)_2 \rightarrow BaO + 2NO + 3/2O_2$ 



### Distribution of NO and NO<sub>2</sub> Desorption Features Very Sensitive to BaO Loading



- Al<sub>2</sub>O<sub>3</sub>: bidentate nitrates
- 2%-BaO/Al<sub>2</sub>O<sub>3</sub>:
  bidentate nitrates (BN)
- 8%-BaO/Al<sub>2</sub>O<sub>3</sub>: bidentate nitrates (BN) + ionic nitrates (IN) [BN>IN] (very little NO<sub>2</sub> adsorption on BaO-free Al<sub>2</sub>O<sub>3</sub>)
- 20%-BaO/Al<sub>2</sub>O<sub>3</sub>: bidentate and ionic nitrates [BN<IN] (virtually no Al<sub>2</sub>O<sub>3</sub> surface is BaO-free)





## NO<sub>2</sub> and NO<sub>2</sub>+H<sub>2</sub>O on BaO/Al<sub>2</sub>O<sub>3</sub>: <sup>15</sup>N Solid State NMR



Three types of nitrates:

• on alumina (easily removed by  $H_2O$ );

- Surface nitrates (peak sharpens with  $H_2O$  addition);
- bulk-like nitrates (unchanged by  $H_2O$  addition)



## Sulfation followed by in situ NO<sub>2</sub> TPD



While  $SO_2$  monotonically decreased the desorption from 'bulk' nitrates,  $NO_2$  adsorption on 'monolayer' nitrates is unaffected at low sulfur levels. In a similar way, performance degradation is minimal at low sulfur exposures but progresses rapidly once begun.



## Mechanistic Studies During Rich Regeneration: Nitrogen-Balance Experiments

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## **Experimental Details**

- Quartz reactor: 1"OD x 7/8" id; Temp. control via programmable furnace
- FTIR: 2 meter, 200 cc cell at 50 °C, 1 atm --- NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O .... Repeat time as fast as 2 seconds
- Micro GC with 3 independent columns; Used for detection of N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> 10-20 lean-rich cycles needed to collect GC data
- Chemiluminescent NOx Analyzer

Standard Gases:	280 ppm NO						
	10% CO <sub>2</sub>						
	$0 - 25 ppm SO_2$ (to date, none used)						
	0-2% H <sub>2</sub> O (to date, none used)						
Lean Phase:	4-8% O <sub>2</sub>						
Rich Phase:	4% CO or 1.3% H <sub>2</sub>						

Flow: 1-3 slm over (3-7 cc) catalyst brick – Space velocity: 8,000-50,000/Hr 3 way solenoid valves – lean and rich gas mixtures always flowing



## Lean NOx Trap Catalysis System



## **Testing 'Degreened' UMICOR Monolith**

**Conditions:** 

2 SLM flow over 6.9 cc catalyst brick (2.08 cm long; 2.06 cm dia) SV ~ 17000/Hr

Temperature ~250 °C

Gases: He + 280 ppm NO flowing at all times; 70 seconds lean:  $4\% O_2$ Variable rich cycle (2-20 seconds):  $1.3\% H_2$ No water added, but it is formed from  $H_2$ oxidation during the rich cycle



## Umicore GDI LNT: ORNL Elemental Screening Results

- Green
  - Washcoat:
    - Zr, Ce
    - La additive/impurity
  - Precious Metals:
    - Pt, Pd, Rh in descending concentration
  - Sorbate (Group I, II):
    - Ba major
    - Sr, Na detected as minors/impurities

- Degreened: 16 hrs,700°C
  - Washcoat:
    - Zr, Ce
    - La additive/impurity
  - Precious Metals:
    - Pt, Pd, Rh in descending concentration
  - Sorbate (Group I, II):
    - Ba major
    - Sr, K, Na detected as minors/impurities

# **Bottom Line:** Umicore LNT chemistry is similar to Three-Way Catalyst with Barium for NOx storage



# Waited until consistent results were obtained in FTIR data





## Example 'steady-state' data



# **3-second rich period insufficient to regenerate LNT**



Time

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 N<sub>2</sub>O formed early in the rich cycle
 Significant

• No NH3

Signficant
 NOx (NO and
 NO<sub>2</sub>) 'puffs'
 when cycled
 rich



# ~6-8 second rich period optimum for regeneration



 $\Delta$  T (sec)

rich cycle • Small amount of NH3

• No NOx (NO

breakthrough!

and  $NO_2$ )

 $\cdot N_2O$  formed

early in the

formation late in the cycle



# Longer rich periods result in significant NH<sub>3</sub> formation



## N<sub>2</sub> readily detected and quantified by GC



# N<sub>2</sub> formation occurs early in the rich cycle, before NH<sub>3</sub>





### N<sub>2</sub> formation maximizes at ~5-6 seconds



# Nitrogen balance > 90%

	Seconds Rich	2	3	4	5	6	7	8	10	13	20
Catalyst Out											
N2	ppm-sec	1277	3118	5450	7886	8736	8815	9020	9349	9017	8733
	μMol N out	3.8	9.3	16.2	23.5	26.0	26.2	26.8	27.8	26.8	26.0
	% NO in	13.4	32.1	55.4	79.2	87.3	87.2	88.1	89	83	74.4
NO	ppm-sec	6273	4428	2468	214	0	0	0	3	8	0
	μMol N out	9.3	6.6	3.7	0.3	0.0	0.0	0.0	0.0	0.0	0.0
	% NO in	32.8	22.7	12.5	1.1	0	0	0	0	0	0
NO2	ppm-sec	8052	6232	3982	683	236	54	1	0	0	0
	μMol N out	12.0	9.3	5.9	1.0	0.4	0.1	0.0	0.0	0.0	0.0
	% NO in	42.1	31.9	20	3.4	1.2	0.3	0	0	0	0
N2O	ppm-sec	368	565	803	999	930	752	806	718	727	597
	μMol N out	0.5	0.8	1.2	1.5	1.4	1.1	1.2	1.1	1.1	0.9
	% NO in	3.9	5.8	8.1	9.9	9.2	7.3	7.8	6.7	<b>6.8</b>	5
NH3	ppm-sec	36	37	83	29	115	90	356	1753	1926	3669
	μMol N out	0.1	0.1	0.1	0.0	0.2	0.1	0.5	2.6	2.9	5.5
	% NO in	0.2	0.2	0.4	0.1	0.6	0.4	1.7	8.2	8.7	15.3
Sum	% Nox Converted	17.5	38.1	63.9	89.2	97.1	94.9	97.6	103.9	98.5	94.7
	% N recovered	92	93	96	94	<b>9</b> 8	95	98	104	99	95
H2O	ppm-sec	31950	43670	52680	61080	69400	76790	83720	97180	98050	122000
	% of total H2 in	123	112	101	94	89	84	81	75	58	47
H2	ppm-sec	0	0	0	0	0	0	0	0	12423	94400
	% H2 in	0	0	0	0	0	0	0	0	7	36

- NOx conversion reaches 90% for 6 seconds.
- NH<sub>3</sub> only becomes a significant product more rich times > 8s.
- N<sub>2</sub>O ~5-10% of NO-in and insensitive to rich time.
- Reductant (H<sub>2</sub>) breakthrough at >10 s rich.



# Distribution of N-containing species with varying rich times

2-20\_Sec\_Nresults--%



Initial Experiments: Compare Product Distributions with H<sub>2</sub> versus CO

- Used 7.2 cc LNT brick (commercial LNT catalyst from a 2004 Ford Mondeo 1.8 SCI – obtained from John Hoard and George Graham, Ford Scientific Research Labs)
- 1 slm for ~ 18000/Hr over Catalyst at 210 °C
- Vary reductant H<sub>2</sub> or CO
- Input 500 ppm NO, look for N<sub>2</sub>
- Dropped O<sub>2</sub> to 2% for simpler N<sub>2</sub> detection



## Nitrogen Balance, Third cycle



- Detected N<sub>2</sub> –
  60% of NOx over cycle to N<sub>2</sub>
- Late NH<sub>3</sub> production as N<sub>2</sub> production drops
- No NOx breakthrough during 'steady-state' reduction phase



### Nitrogen Balance—Third Cycle



- Small N<sub>2</sub> signal only spike on Rich-to-Lean transiton
- Much lower NOx conversion with CO vs H<sub>2</sub> as reductant



## **Summary and Conclusions**

- The morphology of BaO/Al<sub>2</sub>O<sub>3</sub> LNT materials is remarkably dynamic during NOx storage and reduction. A 'monolayer' of Ba(NO<sub>3</sub>)<sub>2</sub> forms on the alumina surface in addition to large bulk Ba(NO<sub>3</sub>)<sub>2</sub> particles.
- As the amount of barium oxide increases, the NOx uptake also increases. However, a significant fraction of the BaO sites (up to 80%) do not take part in the formation of Ba(NO<sub>3</sub>)<sub>2</sub> even after uptake for extended periods.
- and NMR spectroscopies display features that correlate well with these two 'forms' of Ba(NO<sub>3</sub>)<sub>2</sub>. These two forms also appear to decompose in two distinct temperature regimes and give rise to two different desorption products.
- Early stages of sulfur adsorption appears to effect 'bulk' uptake first before 'monolayer' uptake.
- Nitrogen balance experiments show the distribution of N-containing products during rich regeneration. While N<sub>2</sub> and N<sub>2</sub>O form early in the rich phase, extended rich periods lead to the production of significant quantities of NH<sub>3</sub>. Marked differences are observed in the products produced during rich regeneration of production LNTs when comparing reduction by H<sub>2</sub> and CO.



## Future Work

- BaO morphology studies
  - Effects of CO<sub>2</sub> and/or H<sub>2</sub>O on morphology changes during NOx uptake and release. TP-XRD studies to be performed at National Synchrotron Light Source (NSLS) this summer.
  - In-situ TEM studies to watch morphology changes in real time.
  - Effects of additional catalyst components (e.g., ceria as used in CLEERS Umicore material), and alternative support materials (e.g., MgO and MgAl<sub>2</sub>O<sub>4</sub>).
  - Role of Pt/BaO interface for optimum NOx storage.
- Studies of CLEERS Umicore samples
  - CLEERS performance protocol experiments
  - Additional nitrogen balance experiments
    - Varying reductant (1 or more of  $H_2$ , CO, and/or  $C_3H_6$ )
    - Add in  $CO_2$  and  $H_2O$
    - Varying lean times
    - Varying temperatures

